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Analysis of volatile compounds in gluten-free bread crusts with an optimised and validated SPME-GC/QTOF methodology

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ABSTRACT

The aroma of bread crust, as one of the first characteristics perceived, is essential for bread acceptance. However, gluten-free bread crusts exhibit weak aroma. A SPME-GC/QTOF methodology was optimised with PCA and RSM and validated for the quantification of 44 volatile compounds in bread crust, extracting 0.75 g of crust at 60 °C for 51 min. LODs ranged between 3.60 and 1760 μg Kg^{-1}, all the R^2 were higher than 0.99 and %RSD for precision and %Er for accuracy were lower than 9% and 12%, respectively. A commercial wheat bread crust was quantified, and furfural was the most abundant compound. Bread crusts of wheat starch and of japonica rice, basmati rice and teff flours were also quantified. Teff flour and wheat starch crusts were very suitable for improving gluten-free bread crust aroma, due to their similar content in 2-acetyl-1-pyrroline and 4-hydroxy-2,5-dimethyl-3(2H)-furanone compared to wheat flour crust and also for their high content in pyrazines.

1. Introduction

The aroma of bread crust is one of the first attributes sensed when entering a bakery shop. It has been characterised by volatile compounds from Maillard reactions, caramelisation and thermal degradation (Pico, Bernal, & Gómez, 2015), although there can be volatile compounds from lipid oxidation in smaller proportions (Moskowitz, Bin, Elias, & Peterson, 2012). 2-Acetyl-1-pyrroline, generated by Maillard reactions, has been considered the key volatile compound of wheat flour bread crust. Other important volatile compounds include 3-methylbutanal, 2,3-butanedione and 4-hydroxy-2,5-dimethyl-3(2H)-furanone, also from Maillard reactions, along with 2-(E)-nonenal and 2,4-(E,E)-decadienal from lipid oxidation (Zehentbauer & Grosch, 1998).

In the case of gluten-free bread, the sensory quality is barely acceptable, almost notably the texture and the aroma (Pacyński, Wojtasiak, & Mildner-Szkudlarz, 2015). Quality parameters such as nutritional value, rheology of the dough, texture, volume and colour have been widely studied in gluten-free bread (Houben, Höchstötter, & Becker, 2012; Masure, Fierens, & Delcour, 2016). However, there is little knowledge regarding the aroma of gluten-free bread crusts. To our knowledge, only Pacyński et al. (2015) have studied the volatile compounds of gluten-free bread crusts with amino acid – sugar pairs added with the aim of promoting the generation of Maillard compounds and improving the aroma of the crust.

Therefore, the analysis of volatile compounds of bread crust becomes essential in order to improve bread quality, above all of gluten-free bread crusts. In the last decade, solid phase microextraction (SPME) combined with GC/MS has been preferred because it is a quick, simple and solvent-free technique (Thompson-Witrick et al., 2015). Moreover, it only requires a minimal amount of sample, which is important in the case of gluten-free breads that present a poor crust. Focusing on SPME-GC/MS volatile compounds analyses, most researchers have studied the crumb and crust together (Paraskevopoulou, Chrysanthou, & Koutidou, 2012; Plessas et al., 2008, 2011; Poinot et al., 2007, 2008). The study of the volatile compounds from the crust separately from the crumb is very important in order to understand its volatile profile. To our knowledge, only Raffo, Carcea, Castagna, and Magrì (2015) and Pacyński et al. (2015) have studied the volatile compounds of bread crust by SPME-GC/MS, the latter examining gluten-free bread crust. On the other hand, understanding the performance characteristics of the analytical methodology is crucial in order to achieve reliable results, but this information has only been reported for SPME-GC/MS analyses of bread by Raffo et al. (2015). They studied the repeatability, intermediate precision, linearity as well as LOD and

Abbreviations: 2-ACPY, 2-acetyl-1-pyrroline; CAR, carboxen; CCD, central composite design; D, desirability function; DVB, divinylbenzene; DOE, design of experiments; FD, flavour dilution factor; GC/QTOF, gas chromatography/quadrupole-time of flight; HPMC, hydroxyl propyl methyl cellulose; LOD, limit of detection; LOQ, limit of quantification; MSA, method of standard addition; OT, odour threshold; PA, polyacrylate; PC, principal component; PCA, principal component analysis; PDMS, polydimethylsiloxane; R^2, coefficient of determination; Re, relative error; RSD, relative standard deviation; RSM, response surface method; SPME, solid-phase microextraction

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LOQ for volatile compounds analyses in wheat bread crust. However, to the best of our knowledge, the accuracy has not been studied for any SPME-GC/MS methodology; verifying the accuracy is very important for interpreting the quantifications made from these methodologies, since it expresses the closeness of the experimental result to the accepted value (AOAC guideline, 2002). Finally, the optimisation of the methodology before its validation is also imperative so as to ensure that the maximum amount of analyte is extracted, but any optimisation was carried out by Raffo et al. (2015) for the analysis of the volatile compounds of the crust by SPME-GC/QTOF. Moreover, as far as we know, the use of statistical tools such as the Response Surface Method (RSM) has not been reported for the optimisation of SPME methodologies for bread volatile compounds analyses.

Therefore, the first aim of this study was to optimise and validate a SPME-GC/quadrupole-time-of-flight (QTOF) methodology for the semi-quantification (lower limits of detection, since it works in splitless mode) and quantification (higher limits of detection, since it works in split mode) of 44 volatile compounds in bread crust, employing a commercial bread crust sample for this purpose. The quantification of the commercial sample was made using the Method of Standard Addition (MSA). It must be noted that this is the first time that a SPME methodology has been optimised through the use of Design of Experiments (DOE) in the analysis of volatile compounds in bread, specifically with Principal Component Analysis (PCA) followed by RSM. The second goal was to quantify volatile compounds through the MSA of teff, basmati rice, japonica rice and wheat starch bread crusts for the selection of the most suitable gluten-free flour or starch for the improvement of the final aroma of gluten-free bread crust, using wheat bread as a control sample. The choice of the quantified gluten-free bread crusts was made using the semi-quantification method as screening process of oat, quinoa, teff, basmati rice, japonica rice and corn and wheat starch.

2. Materials and methods

2.1. Materials, reagents and standards

For the analytical characterisation of the method, 2-acetyl-1-pyrroline (2-ACPY) was purchased from Eptes (Vevey, Switzerland) and the other 43 pure standards found in Table 1 were purchased from Sigma-Aldrich (Steinheim, Germany). Dichloromethane was obtained from Scharlab (Barcelona, Spain) and methanol was from VWR International (Fontenay-sous-Bois, France). Argon, nitrogen and helium were acquired from Carburos Metálicos (Barcelona, Spain).

2.2. Preparation of standard solutions

2-ACPY solutions were prepared in dichloromethane, as 2-ACPY dimerises in methanol and water. It was necessary to work under inert atmosphere of argon at all times due to the compound's lack of stability to oxygen and moisture. For this reason, dichloromethane was dried in a SDS PS-MD-5 purification system from Düperthal Sicherheitstechnik (Karlstein am Main, Germany). For the other 43 volatile compounds included in Table 1, working solutions of each volatile compound were prepared in methanol. All the solutions were stored in a freezer at −20 °C.

2.3. Sample employed for the development of the SPME-GC/QTOF method

The development and characterisation of the methodology were carried out with the crust of wheat bread purchased from Forvasa (Puçol, Spain). The label indicated that the ingredients were wheat flour, water, salt, yeast and flour improver (wheat flour, anti-caking agent (E-170), emulsifier (E-472e), antioxidant (E-300) and enzymes).

Loaves of bread were cut into slices of 5 cm width, including the ends. The crust was scratched with a knife, taking care not to remove pieces of crumb. Once all the crust was removed, it was frozen with liquid nitrogen and finally it was grounded in an Ika grinder model M20 (Staufen, Germany) for 10 s.

Table 1
LODs and LOQs (in μg Kg^{-1}), repeatability (%RSD) and accuracy (%Re) of the 44 studied volatile compounds with proposed quantitative method. The LODs of the semi-quantitative method are also given.

Volatile compound	LOD split 1:100	LOQ split 1:100	LOD splitless	% RSD intraday	% RSD interday	% Re
2,3-Butanedione	131	438	0.801	2.24	4.60	3.33
Hexanal	62.8	209	2.53	2.39	4.40	1.82
2-Methyl-1-propanol	57.6	192	1.38	0.480	4.60	3.59
1-Methylpyrrol	28.6	95.2	1.49	0.400	0.800	3.15
Heptanal	101	338	1.27	1.65	1.50	3.18
R-Limonene	5.70	19.0	2.54	0.780	6.50	4.14
Pyrazine	54.2	181	3.42	0.750	5.60	1.47
2-Methyl-1-butanol	128	427	0.77	5.75	4.80	2.12
3-Methyl-1-butanol	140	467	0.78	3.96	5.10	0.977
1-Pentanol	402	1340	1.00	6.23	9.00	1.57
2-Methylpyrazine	53.6	179	0.15	0.530	1.30	0.324
Acetoin	476	1586	1.49	2.73	2.90	0.821
2-Octanone	40.2	134	0.34	4.52	4.70	10.9
2,5-Dimethylpyrazine	22.7	75.5	0.18	4.95	3.70	3.27
2,6-Dimethylpirazine	35.0	117	1.39	3.73	4.90	1.93
2-Ethylpyrazine	28.6	95.5	0.24	0.670	2.30	0.847
2-Acetyl-1-pyrroline	12.1	39.9	0.19	1.25	3.21	0.981
2,3-Dimethylpyrazine	25.6	85.3	2.53	0.500	4.10	2.57
1-Hexanol	105	349	0.81	0.760	2.10	1.55
Nonanal	102	341	2.47	2.57	3.70	0.235
2,3,5-trimethylpyrazine	4.70	15.6	1.76	0.570	4.50	1.31
2-Ethyl-3-methylpirazine	8.00	26.6	1.90	0.930	4.30	2.34
Ethyl octanoate	3.60	12.0	0.65	5.39	8.60	2.55
1-Octen-3-ol	8.40	27.9	3.67	3.58	3.50	0.281
Acetic acid	49.3	164	1.62	7.03	1.00	nq[a]
Furfural	50.3	168	3.61	2.38	2.70	7.02
2-Ethyl-1-hexanol	22.6	75.4	2.01	5.17	4.80	0.648
Benzaldehyde	19.7	65.7	1.84	0.830	4.10	0.085
2-(E)-Nonenal	43.6	146	1.91	1.13	3.10	12.2
5-Methyl-2-furaldehyde	87.7	292	0.21	0.130	2.40	3.94
Butyrolactone	743	2477	1.38	4.42	7.40	5.14
2-Acetilpyrazine	15.3	51.0	0.95	1.27	4.90	2.56
Butyric acid	392	1307	0.81	1.31	2.50	1.58
Phenylacetaldehyde	28.50	94.8	0.68	1.32	2.20	0.683
Furfuryl alcohol	66.6	222	1.93	1.84	4.10	nq[a]
2-Methylbutyric acid	225	751	4.46	5.51	1.20	2.58
3-Methylbutyric acid	667	2224	3.17	7.89	1.50	0.229
2,4-(E,E)-Decadienal	25.9	86.3	1.73	5.20	4.30	3.05
Hexanoic acid	1540	5132	0.85	0.120	2.40	0.374
Benzyl alcohol	67.8	226	0.77	0.560	7.20	1.66
Phenylethyl alcohol	48.8	163	2.76	3.91	8.60	0.425
2-Acetylpyrrol	290	966	1.34	3.86	4.90	1.68
4-Hydroxy-2,5-dimethyl-3(2H)-furanone	1755	5851	3.61	3.74	2.70	0.945
4-Vinylguaiacol	985	3284	3.15	3.73	5.20	1.83

[a] nq = not quantified.

2.4. Gluten-free bread formulation: flours, starches, hydrocolloid and yeast

Wheat starch was supplied by Roquette Laisa (Valencia, Spain), corn starch by Miwon Daesang (Seul, Korea) and wheat flour by Harinera Castellana (Medina del Campo, España). Japanica rice flour was purchased from Molendum ingredients (Zamora, Spain), oat flour from Emilio Esteban (Valladolid, Spain), quinoa flour from El Granero Integral (Madrid, Spain) and teff flour from Salutef (Palencia, Spain). Basmati flour was milled from basmati rice from Dacsa (Lisboa, Portugal), employing a grinder model Perten 3300 (Hägersten, Sweden). Hydroxyl propyl methyl cellulose (HPMC) K4M was supplied